Ion mixing of markers in SiO_2 and Si

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The amount of atomic mixing in amorphous SiO_2 and Si is studied by measuring the redistribution of thin metal markers due to irradiation with 300-keV Xe^+ ions. In SiO_2, the mixing efficiency appears to be independent of the chemical nature of marker atoms and can be explained in terms of a linear cascade model. In Si, the mixing is found to correlate with thermally activated diffusivities of the marker species.

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A question of primary importance in the study of ion mixing in solids is to what extent various processes contribute to the atomic transport. To date, most basic experimental studies have considered metal-silicon systems, either in bilayer configurations (several hundred angstroms of metal deposited on Si) or in marker configurations (~ 10 Å of metal embedded several hundred angstroms deep in Si).[1] In most cases, it was found that below about room temperature the mixing of such systems is almost independent of the temperature during irradiation. Also, in this temperature regime, bilayer samples exhibit monotonically varying composition across the mixed layer. Therefore, it has been suggested that mixing at low temperatures is dominated by purely collisional events.[2,3]

There are two considerations, however, that lead one to question this conclusion. Firstly, the mixing that was observed for Au markers in Si is about twice that of Pt markers in Si; similarly, Ge markers mix twice as much as Ni markers.[2] Collisional mixing of marker pairs of such similar mass and atomic number should have similar magnitudes, assuming that they have similar displacement threshold energies.[4] Secondly, the most detailed calculations of collisional mixing that have been published[5] yield magnitudes for the mixing of Pt markers in Si that are a factor of 50 lower than those observed experimentally.

One way to explore this issue further is to investigate ion mixing of markers in very dissimilar media. If the observed mixing is not simply collisional, but also includes other mechanisms (e.g., thermally activated migration) these mechanisms are likely to change significantly from one medium to another.[6] They are also likely to affect the different marker species in different ways depending on the particular chemistry or metallurgy of the marker/medium systems.[6] We have measured the irradiation-induced mixing of a series of metal markers buried in amorphous SiO_2. Also, for comparison, the mixing of three of these metals as markers was measured in pure amorphous Si. Amorphous SiO_2 is clearly of interest because the thermal diffusivities of most elements in SiO_2 are expected to be orders of magnitude lower than they are in Si.[7,8] Measurements of bilayer systems consisting of metals and SiO_2 have already been reported.[9] In these, the profiles of mixed metal in the SiO_2 and the temperature dependence of the mixing were consistent with purely collisional mixing up to at least 300 K.

The metals Ti, Co, Ni, Hf, W, Pt, and Au were selected as the markers. They were chosen to cover a wide range of atomic masses and chemical reactivities with Si and SiO_2. Samples were prepared by electron gun deposition of the metal on previously oxidized Si, followed by chemical vapor deposition (CVD) of SiO_2 at 100 °C. In addition, for three elements (Ti, W, and Pt) it was possible to make samples by depositing ~ 10 Å of metal on thermally grown SiO_2, covering it with 250 Å of silicon, and subsequently oxidizing the Si in steam at 780 °C for 15 min. In these systems, it was observed by backscattering spectrometry (BS) that even though some metal diffused into the Si initially, the metal distribution was restored to its original position by the advancing SiO_2-Si interface. In all cases, the marker thickness was ~ 10 Å and the SiO_2 overlayer was ~ 600 Å thick. Also, markers of W, Pt, and Au in Si were prepared by sequential electron gun deposition of several hundred angstroms of Si, followed by ~ 10 Å of the marker element, and then 600 Å of Si.

The samples were irradiated with 300-keV Xe ions at 80 and 300 K: all were irradiated to a fluence of 1.5×10^{16} ions/cm^2, while W, Pt, and Au markers in both Si and SiO_2 were also irradiated to a range of fluences from 2×10^{15} to about 3×10^{16} ions/cm^2.

The amount of redistribution of the markers was deduced from 2-MeV helium ion backscattering spectrometry with the samples tilted about a vertical axis by 70.5° with respect to the normal to the incident beam. The detector was mounted in a vertical plane through the beam, at a scattering angle of 170°. Spectra were recorded for each sample before and after irradiation. In addition, samples without markers, but which otherwise were of identical composition and received identical treatment, were also analyzed, after irradiation. The spectra from the latter were subtracted channel-by-channel from those for the marker samples to give clean marker signals. The second central moments, or variances, Ω^2, of the marker peaks were calculated numerically by taking into account all data points exceeding 5% of the peak maximum. This has the effect of substantially reducing the random uncertainties relative to the case when all channel counts down to about zero are considered,[10,11] while the error incurred in the absolute magnitude of Ω^2 was small. The magnitude of mixing was found from the variance of the redistribution due to ion irradiation, given by

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TABLE I. Variances of mixing, σ^2 (10^3 Å^2) in thermal and CVD SiO_2 for 300 keV, 1.5×10^{16} Xe^+ ions/cm^2, 300 K.

Medium \ Marker	Ti	W	Pt
SiO_2, thermal	7.1 ± 0.8	19.4 ± 2.1	18.8 ± 2.0
SiO_2, thermal & CVD	6.1 ± 0.7	18.4 ± 2.0	21.5 ± 2.3

$$\Omega^2=\Omega^2_{\text{irr}}-\Omega^2_{\text{unirr}}, \quad (1)$$

where Ω^2_{irr} is the variance after the irradiation and Ω^2_{unirr} is the variance before the irradiation. In all cases, the profiles after mixing were approximately Gaussian. The variance Ω^2 in energy was then converted to a variance σ^2 in depth, assuming a density of 2.3×10^{22} molecules/cm^3 for SiO_2 and tabulated stopping cross sections for ^{4}He in SiO_2.

We found that the extent of mixing is the same for the markers covered by CVD SiO_2 as it is for those covered by thermally grown SiO_2. This is illustrated in Table I, where σ^2 is given for the Ti, W, and Pt markers with overlayers prepared by both techniques, irradiated at 300 K to a fluence of 1.5×10^{16} ions/cm^2. These results show that if there are structural or compositional differences between samples prepared by the two techniques, they do not influence the mixing efficiencies significantly.

The magnitudes of the mixing of all seven marker species in SiO_2, and the three markers in Si, by 300-K irradiations to 1.5×10^{16} ions/cm^2 are presented in Table II. We note that in SiO_2 the values of σ^2 for markers with similar atomic number are fairly similar—unlike in the case of a Si matrix. Also, we note that σ^2 appears to vary smoothly with atomic number, again in contrast with observations for markers in a silicon matrix.[2]

The magnitude of mixing at 300 K observed for three marker species (W, Pt, and Au) in both SiO_2 and Si is plotted against irradiation fluence in Fig. 1. The uncertainty in the absolute value of σ^2 at a fluence of 1×10^{16} ions/cm^2 was estimated to be $\pm$ 11%, deduced from the variations in five independent measurements for a W marker in SiO_2. Consider first the results for the markers in SiO_2 (filled symbols). The data points for all three elements are consistent with a single unit-gradient linear relationship with ion fluence. Now consider the mixing for markers embedded in Si (open symbols). The experimental points for the marker elements follow lines of gradient unity, but the lines are well separated: the data for Pt are about a factor of 3.5 higher than that for W, while the data for Au are about a factor of 6 higher than that for W. In addition, based on the results of similar measurements conducted with a single irradiation dose (1×10^{16} ions/cm^2) at 80 K, we find that the same trends appear to hold at lower temperatures. The values of σ^2 (in 10^3 Å^2) for W, Pt, and Au markers in Si were 7.5, 24, and 40, respectively, compared with 6.6, 25, and 46 at 300 K. In SiO_2, the results for these markers were (again in units of 10^3 Å^2) 11, 15, and 8, compared with 11, 16, and 9.9 at 300 K. The variation of mixing between 80 and 300 K is thus insignificant in those cases.

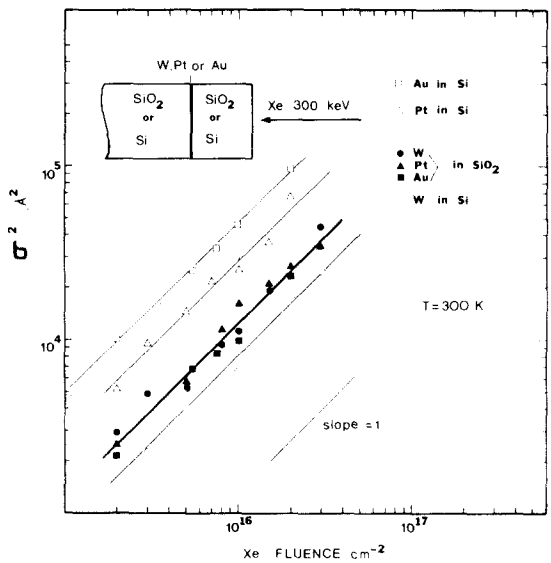

FIG. 1. Variances of mixing, σ^2, plotted as a function of dose for 300-keV Xe^+ irradiation at room temperature into Si and SiO_2 containing W, Pt, and Au markers.

TABLE II. Variances of mixing, σ^2 (10^3 Å^2) of different markers in SiO_2 and Si for 300 keV Xe^+, 1.5×10^{16} ions/cm^2, 300 K.

Marker							
Atomic number Z	Ti 22	Co 27	Ni 28	Hf 72	W 74	Pt 78	Au 79
SiO_2	6.6 $\pm$ 0.7	9.0 $\pm$ 1.0	10.1 $\pm$ 1.1	16.6 $\pm$ 1.8	19.2 $\pm$ 2.1	20.2 $\pm$ 2.2	18.0 $\pm$ 2.0
Si					14.5 $\pm$ 1.6	37.0 $\pm$ 4.0	60.0 $\pm$ 7.0

Previous measurements of the mixing of Pt markers in Si[2,11] can be compared with these results after correcting for the different marker depths. For this purpose, those data were scaled by the appropriate ratios of F_D, the energy per unit depth, deposited by nuclear processes.[12] The results (in 10^3 Å^2) for a fluence of 1×10^{16} ions/cm^2 are 18 ± 4 and 23 ± 4 from Refs. 2 and 11 respectively and 24 ± 2.5 in the present work. The difference between the amount of mixing for Au in Si and Au in SiO_2 was also demonstrated directly with a special sample consisting of a Au marker lying at a Si-SiO_2 interface. After irradiation to a fluence of 1×10^{16} ions/cm^2 at 80 K, the Au profile became clearly asymmetric, extending preferentially into the Si (see Fig. 2). The observed asymmetry cannot be explained by differences in F_D. Interpolations of the calculations by Winterbon[13] show that F_D at the Si-SiO_2 interface for 300 keV Xe is approximately the same in the two media.

We have determined that the irradiation-induced spreading in amorphous SiO_2 of markers of nearly similar masses is the same to within experimental error, while differences as large as a factor of 6 are observed for these markers in amorphous Si. Within the binary collisional model, the mixing of an impurity species depends on the collision cross sections, recoil ranges, and E_d, the minimum displacement energy of the impurity atoms in the particualr medium (see, e.g., Ref. 4). Therefore, for a fixed displacement energy, mix-

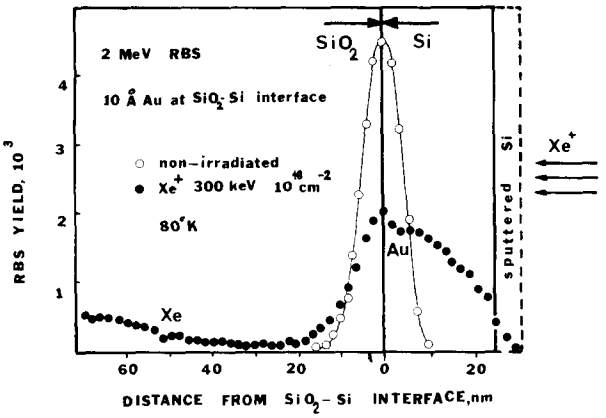

FIG. 2. Backscattering spectrum of a 10-Å Au marker located at the SiO_2-Si interface: before (○) and after (●) irradiation with 300 keV Xe^+, 1×10^{16} ions/cm^2 at 80 K.

ing efficiencies predicted by this model for W, Pt, and Au would not vary by more than 5%.[4] In fact, the experimental points for these elements in SiO_2 lie close enough to be consistent with a common value of E_d. However, to explain the large differences observed in Si, one would require that E_d vary considerably between different marker species in that medium. For example, between Au and W it must change by about a factor of 4. In principle, this possibility cannot be ruled out, as the actual displacement energies for these elements in Si and SiO_2 are unknown. But it seems unlikely that the displacement energies for different impurities vary so drastically in Si when they appear to be so similar in SiO_2. It is interesting to note that the self-displacement energies for the elemental materials W, Pt, and Au are all close to 36 eV (within 15%).[12]

On the other hand, we observe that for these marker systems, there is a correlation between the measured marker broadenings under ion irradiation at low temperatures and their thermally activated diffusivities. The extent of mixing appears to be enhanced for fast diffusers, and reduced for slow diffusers. Based simply on the lowest eutectic temperatures for these markers with Si,[14] one would expect $D_{Au} > D_{Pt} \gg D_W$. Published data for Au and Pt in crystalline Si are as follows: for Au the pre-exponential factor, D_0 is 10^{-3} cm^2/s, and the activation energy E is 1.1 eV.[7] For Pt, $D_0 = 1.5\times10^2$ cm^2/s and $E = 2.2$ eV.[15] Thus the diffusivity of Au in Si is higher than that for Pt in Si for temperatures up to 1070 K. In SiO_2, the diffusivities of these three elements are expected to be low; for example, the ratio of diffusion constants for Au in Si and SiO_2, D_{Si}/D_{SiO_2} is as large as 10^9.[15] As our samples consisted of amorphous rather than crystalline Si, and the concentrations of the marker atoms exceeded the solid solubility for these elements in Si and SiO_2, the above data may not be strictly appropriate for our systems. Therefore we measured the broadening of the markers in our samples under thermal annealing at three temperatures (300, 600, and 900 °C). We found that indeed the Au and, to a lesser extent the Pt, diffused very rapidly in the Si at a few hundred °C, while the W, as well as all three markers in SiO_2 were virtually immobile up to at least 900 °C.

Thus, in conclusion, the large variations in the marker spreadings found for Si, relative to the essentially uniform mixing that we have observed in SiO_2, are difficult to explain solely in terms of existing binary collision cascade models. The apparent correlation between the thermal diffusion properties of the marker systems and their spreading under ion irradiation suggests that noncollisional atomic displacements may also contribute. One example of such processes that, in principle, would promote fast diffusers to relocate preferentially under ion bombardment is radiation-enhanced diffusion of defects in a zero activation-energy regime[16]; another possibility is the displacement of impurity atoms as a result of some kind of cooperative motion of matrix atoms induced by a high energy-density cascade.[17] One cannot, however, identify a particular mechanism on the basis of our present experiments alone. Additional measurements in other host media and the correlation of the results with the physical or chemical properties of the marker/host combinations are needed to clarify the issue.

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[1] S. Matteson and M-A. Nicolet, Ann. Rev. Mater. Sci. **13**, 339 (1983).
[2] S. Matteson, B. M. Paine, M. G. Grimaldi, G. Mezey, and M-A. Nicolet, Nucl. Instrum. Methods **182/183**, 43 (1981).
[3] J. W. Mayer, B-Y. Tsaur, S. S. Lau, and L. S. Hung, Nucl. Instrum. Methods **182/183**, 1 (1981).
[4] S. Matteson, B. M. Paine, and M-A. Nicolet, Nucl. Instrum. Methods **182/183**, 53 (1981).
[5] P. Sigmund and A. Gras-Marti, Nucl. Instrum. Methods **182/183**, 25 (1981).
[6] Y. Adda, M. Beyeler, and G. Brebec, Thin Solid Films **25**, 107 (1975).
[7] H. F. Wolf, *Semiconductors* (Wiley, New York, 1971).
[8] M. Ghezzo and D. M. Brown, J. Electrochem. Soc. **120**, 146 (1973).
[9] T. Banwell, B. X. Liu, I. Golecki, and M-A. Nicolet, Nucl. Instrum. Methods **209/210**, 125 (1983).
[10] B. M. Paine, M-A. Nicolet, and T. C. Banwell, in *Metastable Materials Formation by Ion Implantation*, edited by S. T. Picraux and W. J. Choyke (North-Holland, New York, 1982), MRS Symposia Proceedings, Vol. 7, p. 70.
[11] B. M. Paine, J. Appl. Phys. **53**, 6828 (1982).
[12] H. H. Andersen, Appl. Phys. **18**, 131 (1979).
[13] K. B. Winterbon, *Ion Implantation Range and Energy Deposition Distributions* (Plenum, New York, 1975), Vol. 2.
[14] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[15] J. A. Keenan and G. B. Larrabee in *VLSI Electronics: Microstructure Science*, N. Einspruch, Series edited by G. B. Larrabee (Academic, New York, 1983), Vol. 6, p. 1.
[16] G. T. Dienes and A. C. Damask, J. Appl. Phys. **29**, 1713 (1958).
[17] R. S. Averback, in *Proceedings of the Workshop on Ion Mixing and Surface Layer Alloying*, edited by S. T. Picraux and M-A. Nicolet, Sandia Report SAND83-1230, 1983, p. 10.